

Chapter 5

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Title:

Separations vs. Sustainability – there is no such thing as a free lunch.

Chapter description:

Separation operations in chemical processes are generally “uphill” tasks – defying natural tendencies. Historically, such separations have been accomplished by applying generous portions of fossil energy and materials, leaving behind a large environmental footprint. In this chapter, progress in reducing this footprint will be discussed with examples in biofuel production, desalination, and carbon dioxide capture.

1. The separations dilemma and imperative

Industrial separation processes have a significant energy and environmental footprint. In the 2005 report “Materials for Separation Technologies: Energy and Emission Reduction Opportunities”, the U.S. Department of Energy’s Oak Ridge National Laboratory (ORNL) estimated that separation processes account for 22% of all in-plant energy usage in the U.S. (2). The thermally-driven processes of distillation, evaporation, and drying accounted for 49%, 20%, and 11%, respectively, of the separation energy usage. In the chemicals, petroleum refining, forest products, and mining industries, separation processes account for an even higher fraction of in-plant energy usage, about 47%, and consume over 98% of the separation energy used by U.S. industries. The ORNL report concluded the most significant reductions in energy usage could be achieved by replacing energy-intensive processes like distillation with low-energy separation systems such as membranes, extraction, sorption, or synergistic hybrid systems of low- and high-energy systems.

The ORNL report highlighted the following separation problems as being “High-Energy Distillation Processes with Potential for Replacement with Lower-Energy Alternatives”:

1. Olefin-paraffin separations: ethylene/ethane, propylene/propane, etc.
2. Removal of organic compounds from water where azeotropes are formed: ethanol, isopropanol, sec-butanol, etc.
3. Recovery of dilute organics from water: acetic acid, ethylene glycol, methanol, many high-boiling polar organic compounds

4. Cryogenic air separation
5. Polyol separations: ethylene glycol/diethylene glycol, ethylene glycol/ propylene glycol
6. Isomer separations

Also in 2005, the National Research Council (NRC) of the National Academies issued the report “Sustainability in the Chemical Industry: Grand Challenges and Research Needs”, identifying eight challenge areas for chemical industry sustainability (3). The report highlighted the need for advances in efficient chemical separations, especially the development of effective alternatives to distillation. The recovery of chemicals from relatively dilute aqueous solutions, such as fermentation broths or wastewaters, and the separation of carbon dioxide were specifically highlighted. As with the ORNL report, the need for alternatives to distillation, long the workhorse separation technology of the chemical and biofuels industries, was emphasized in the NRC report. In addition to the energy-related environmental impact of separation processes, the ability to achieve environmental objectives is hindered by the inherent energy demand of conventional separation technologies. For example, the U.S. Environmental Protection Agency (USEPA) recently finalized a new definition of Solid Waste intended to promote the reuse/re-processing of 18 solvents to reduce the use of virgin solvents, cutting energy and waste, particularly in the pharmaceutical, paint and coating, plastic and resin, and basic organic chemicals sectors (4). However, replacement of virgin solvents requires the application of separation technologies to recover those solvents from their mixtures with other solvents and/or water used in the industrial process and to purify the solvents to meet process specifications.

The greatest potential advancement in separation processes would be to minimize their usage. That is to say, begin with a raw material or alter the production system preceding the separation step such that the separation requirement is eliminated or reduced. These concepts are embodied in several of Anastas and Zimmerman’s twelve Principles of Green Engineering, particularly Principle #3: “Design for Separation” (5). Intuitively, we understand that a higher product concentration will make recovery of a unit of that product less demanding. Unfortunately, the separation step is often considered later in the product/process development timeline. The task of just designing a workable chemical or biological reaction scheme is often daunting enough. However, ignoring or delaying design of the separation step imperils both the economic and environmental viability of the enterprise.

The economic impact of product concentration is clearly demonstrated in what has been termed a “Sherwood plot”, relating the selling price of a variety of purified materials to the concentration of the materials in the initial matrices from which they are being separated (1, 6-10). The most widely referenced Sherwood plot is from Grüber’s book “Technology and Global Change” (1), shown in [Figure 1](#). Grüber’s Sherwood plot illuminates the dramatic effect initial concentration has on the selling price of a commodity or the cost of contaminant removal across a range of material types. The prices in [Figure 1](#) embody more than just the cost of separation steps, but, due to the significance of separation processes in total cost, it is easy to imagine that separation costs are similarly correlated with initial concentration. For example, the capital cost of separations and supporting facilities as a fraction of total capital costs has been estimated to range from 33% for a typical chemical plant to 70% for a refinery or bioprocess facility (9). As a result, improvements in both the energy usage, material usage, and capital cost of separation processes would go a long way to improving the financial and environmental bottom lines for chemicals and materials.

Unfortunately, a chemical separation requires energy to accomplish because, in general, Mother Nature wants to mix things up. In thermodynamics, this means the Gibb’s Free Energy of mixing is usually negative. In fact, the minimum work (w_{min}) required to accomplish a separation is equal to the negative of the Gibbs Free Energy of mixing (Δg_{mix}^*):

Equation 1

$$w_{min} = -\Delta g_{mix}^* = \Delta h_{mix} - T_0 \Delta s_{mix}$$

Where Δh_{mix} is the heat of mixing, Δs_{mix} is the entropy of mixing, and T_0 is the temperature. The minimum work to separate a mixture of n components into pure streams of each is calculated as:

Equation 2

$$w_{min} = -T_0 R \sum_{i=1}^n x_i \ln(\gamma_i x_i)$$

Where γ_i and x_i are the activity coefficient and mole fraction, respectively, of component i in the feed to the separation unit and R is the gas constant (8.314 J/mol·K). The product ($\gamma_i x_i$) is the activity (a_i) of the component. For ideal binary mixtures of compounds A and B (i.e. $\gamma_i = 1$), [Equation 2](#) ~~Equation 2~~ simplifies to:

Equation 3

$$w_{min} = -T_0 R [x_A \ln x_A + (1 - x_A) \ln(1 - x_A)]$$

In cases where pure component A is recovered with a specific degree of recovery (Y_A) from an ideal binary mixture, the minimum work required per mole of pure component A recovered is calculated as (11):

Equation 4

$$w_{min} = \left[\frac{1}{Y_A} \ln(1 - Y_A) \right] RT_0 \ln(x_A)$$

This relationship, plotted in [Figure 2](#) ~~Figure 2~~, demonstrates the rapid increase in minimum work as the concentration decreases or as the fraction of recovery increases. Later in this chapter, the actual work for several separations will be discussed. The energy required for some separations is near the thermodynamic minimum, while most are far, far higher than the minimum. However, for all, the general behavior illustrated in [Figure 2](#) ~~Figure 2~~ is retained.

2. Methods of analysis

The separation processes within a chemical process are selected and designed using a variety of criteria, with the criterion used in a specific situation established from the information set available and the priorities of the organization. In most cases, the almighty bottom line, cost, drives process decisions, including separation decisions. Ideally, sufficient information and organizational motivation would exist to determine the life cycle impact of separation process options. Less refined analyses rely on comparisons of energy intensity, material intensity, or waste intensity – the amount of each category per unit of product recovered or purified. This may be appropriate when evaluating the effect of design variables within a given separation technology rather than between technology platforms. Because each form of energy, material, and waste has a different value and impact, other refinements are included. For example, comparing a process that relies on thermal energy to one driven by mechanical work, like a natural gas-fired boiler vs. an electrically-powered heat pump. This requires more than a simple energy

input comparison. To this end, energy intensity may be further scrutinized by converting all energy inputs into a common unit, such as the primary energy or fuel equivalents required (i.e. MJ-primary/kg-product or MJ-fuel/kg-product) or greenhouse gas (GHG) equivalents released (kg- CO₂-equivalents/kg-product) (12, 13).

Exergy destruction has been proposed as a metric of process sustainability. Exergy is the maximum useful shaft work that could be obtained from a system at a given state in a specified environment without violating any laws of thermodynamics (14). Irreversibilities in a process result in a loss in work potential, referred to as exergy destruction. As noted by Çengel, the difference between the exergy and the actual work performed “represents the room engineers have for improvement” (14). Although valuable, exergy analyses have not been commonly used to evaluate separation schemes (15, 16). In a 2013 mini-review, Luis reported on the evolution of exergy analyses in chemical engineering literature and highlighted the past and future potential for using exergy analyses in separation process design (15). She concluded that 10-20% of exergy losses arise in the separation stages of chemical manufacturing while 65-90% were due to the irreversibilities in chemical reactions (15). Nevertheless, there are opportunities for reducing the exergy losses in the separation stages due to the high thermodynamic inefficiency of many distillation systems, particularly those with close boiling mixtures (17).

This leads to the definition of a “2nd Law Efficiency” (η) for the generic steady state separation process depicted in [Figure 3](#) as the ratio of the minimum work to the actual work:

Equation 5

$$\eta = \frac{w_{min}}{LW + w_{min}}$$

Where LW is the lost work, or destroyed exergy, defined as (18):

Equation 6

$$LW = \sum_{\substack{\text{streams,} \\ \text{heat,} \\ \text{work} \\ \text{in}}} \left[\dot{N}(h - T_0s) + Q \left(1 - \frac{T_0}{T_s} \right) + W_s \right] - \sum_{\substack{\text{streams,} \\ \text{heat,} \\ \text{work} \\ \text{out}}} \left[\dot{N}(h - T_0s) + Q \left(1 - \frac{T_0}{T_s} \right) + W_s \right]$$

Where \dot{N} is the stream molar flow rate, h and s the enthalpy and entropy of the stream, respectively, T_0 and T_s the temperature of the reference surroundings and heat source (or sink), respectively, Q the heat flow, W_s the shaft work. As noted by Demirel, only zero lost work has no impact on the environment: “lost work causes the inefficient use of energy (loss of exergy), and environmental cost due to (i) discharging lost exergy into the environment, and (ii) the depletion of natural resources because of inefficient use of fossil fuels.” (17) Thus, unless all of the environmental, risk, and societal costs can be accounted for, simple financial cost calculations cannot capture the true “cost” of a separation system.

3. Separation alternatives

Distillation

As noted earlier, distillation is the dominant separation process in the chemical industry. This is due to the “simplicity” of design and operation as well as the economies of scale offered by distillation relative to many of the alternative separation processes. Two books by Henry Kister, “Distillation Design” and “Distillation Operation” are recommended reading for those seeking to understand both the fundamental and practical aspects of distillation systems (19, 20). The leading drawback to distillation is the reliance on high quality energy to provide heat to the reboiler and the removal of heat in the condenser at a lower temperature (schematic shown in [Figure 4](#)). This combination results in poor energy efficiencies and dreadful 2nd Law efficiencies, particularly for close-boiling mixtures. For example, η is only 5% for olefin/paraffin separations (e.g. ethylene and propylene production), 12% in crude oil units, and 18% in cryogenic air distillation (21). As the cost of fossil fuels has increased, so too has the operating cost of distillation, creating opportunities for alternative separation technologies. Those alternatives include: liquid-liquid extraction, gas stripping, adsorption, absorption, membrane separation, crystallization, and combinations thereof.

Although distillation is an established technology, there are still opportunities for improvement. A recent review by Kiss provides an overview of many of these opportunities (21). Thermally linking the reboiler and condenser is a popular concept for improving distillation efficiency. This requires the use of a heat pump to upgrade the heat released in the condenser to be useful in the reboiler. All of the heat pump concepts add complexity and capital cost with the goal of reducing energy usage and operating cost. The most straightforward heat pump concept for distillation, vapor compression (VC), mimics the classic design commonly used in household heat pumps/air conditioners: a working fluid/refrigerant is circulated in a closed loop using a compressor and expansion valve, where the evaporator of the heat pump is the distillation condenser and the heat pump condenser is the distillation reboiler. With this closed loop type of heat pump, the distillation process streams and the heat pump streams are physically separated, with only heat exchange.

Another popular heat pump concept, if not widely adopted, is the direct use of the overhead vapor as the heat pump working fluid, an open cycle heat pump termed mechanical vapor recompression (MVR). In MVR, the compressor raises the pressure of the overhead vapor to the point where it will condense at a temperature sufficient to drive the reboiler. This has the advantage that the reboiler heat exchanger serves as both the reboiler and the condenser. One disadvantage is the process vapor may not be the most efficient working fluid for the temperatures involved. Nevertheless, primary energy savings over 50% are anticipated (21).

The coefficient of performance (*COP*) for an ideal heat pump is defined as the amount of heat moved divided by the shaft work required:

Equation 7

$$COP_{ideal} = \frac{Q_C}{W_S} = \left[\frac{T_{hp,C}}{T_{hp,C} - T_{hp,E}} \right]$$

While the actual *COP* observed is:

Equation 8

$$COP_{actual} = \frac{Q_C}{E_{hp}} = \eta_{hp} \frac{Q_C}{W_S} = \eta_{hp} \left[\frac{T_{hp,C}}{T_{hp,C} - T_{hp,E}} \right]$$

Where Q_C is the heat released in the condenser of the distillation column (J/s), W_S is the work performed by an ideal heat pump (J/s), E_{hp} is the electricity consumed by an actual heat pump (J/s), $T_{hp,C}$ and $T_{hp,E}$ are the temperatures (in Kelvin) of the heat pump condenser and evaporator, respectively, and η_{hp} is the heat pump efficiency factor (η_{hp} ranges from 0.5 to 0.75) (22-24). The quantity in the brackets in [Equation 7](#) is the Carnot efficiency. The difference between $T_{hp,C}$ and $T_{hp,E}$ is the temperature lift. Heat transfer resistances result in a heat pump temperature lift higher than simply the difference between the bottoms and overhead temperatures in the distillation column, thereby reducing the *COP*.

So, just how much energy can a heat pump save? Take the distillation separation of a mixture of methanol and water at atmospheric pressure. Assuming almost pure methanol in the overhead and almost pure water in the bottoms, the overhead temperature is about 65 °C (338 K) and the bottoms temperature is 100 °C (373 K) for a temperature lift of 35 K. According to [Equation 7](#), COP_{ideal} is 10.7. Assuming $\eta_{hp}=0.7$ and that there is a 5 °C minimum approach in each heat exchanger (i.e. $T_{hp,C}=378$ K and lift = 35+2×5= 45 K), COP_{actual} is 5.9 – 45% lower than the ideal. Thus, 1 unit of electrical energy results in 5.9 units of thermal heat being upgraded. The average efficiency of the fossil-fuel powered electrical power grid results in 0.37 units of electrical energy delivered per unit of higher heating value (HHV) of primary energy source consumed (average for US fossil fuel-powered grid in 2011 (25, 26)). This means the heat pump moves 2.18 units of heat to the reboiler per unit of primary energy consumed. For a normal steam generator/reboiler system, 0.85 units of heat are delivered to the reboiler per unit of primary energy converted. As a result, the heat pump primary energy efficiency is 2.6 times that of a steam-heated reboiler. The bottom line, then, for this example of methanol/water separation is that primary energy usage could be reduced 61% by using a closed loop heat pump.

A number of additional factors must be considered to determine if the energy savings would result in financial savings (27, 28). With such high energy savings, it would seem that heat pumps would be more widely utilized in the chemical industry. One reason they are not is that most heat pump concepts add a piece of rotating equipment (the compressor), with all of the added operational costs and downtime risks, to a unit operation that did not already have that type of equipment. On top of that, this added equipment is relatively pricey, meaning the capital cost vs. operation cost payback period may be longer than with other improvements. Humans, particular corporate boards and investors, are not so keen on delayed gratification.

Other distillation process options for improved energy efficiency range from simple to advanced concepts. On the simpler end of the spectrum: adding a feed/bottoms heat exchanger if the feed is at a much lower temperature than the bottoms liquid. One step up is to split the feed into two streams, heating only one using the available bottoms heat and feeding the two feed streams to optimized points on the column (29). The next leap in complexity is similar in concept to a multi-effect evaporator, the feed stream would be split into “n” streams and each would be fed to a separate distillation column operated at a pressure so as to enable the exchange of heat between the reboiler and condenser of different columns in the cascade (28, 30). In another concept, termed “heat integrated distillation column” (HIDiC), the stripping and rectifying sections of the distillation column are operated at different pressures by compressing the overhead vapor from the stripping column (31-33). This is akin to an MVR heat pump, except that the rectification and stripping sections operate at different pressures and these sections are in direct heat exchange to most efficiently affect heat and mass transfer, as opposed to just the condenser and reboiler operating at different pressures. For multi-component mixtures, an advancement receiving significant attention is combining the multiple distillation columns into a single, divided wall column (DWC) allowing for efficient heat transfer (21, 31, 34, 35). Similarly, for processes

involving a reaction step and a distillation step, combining the two into one reactive distillation unit may be more efficient if there is an intermediate bottleneck in one of the two steps. On the more exotic end of the spectrum is the replacement of the fixed vertical distillation column with a rotating bed/contactor to utilize centrifugal forces (“HiGee” technology) to enhance mass transfer (21, 36).

Extraction - Liquid-Liquid Extraction, Gas Stripping, Adsorption, Absorption

The separation processes of liquid-liquid extraction, gas stripping, adsorption, and absorption all have one thing in common: one or more components of the initial stream are transferred to a mass separating agent (MSA) and subsequently recovered from that MSA. The MSA may be regenerated *in situ* or in another device. The latter is depicted in a continuous mode of operation in [Figure 5Figure 5](#). The form of the MSA: gas, liquid, or solid, determines how we refer to the process and how the separation scheme is designed. For example, a liquid or gas MSA is more likely to be operated continuously while a system based on a solid MSA will most likely involve an MSA-filled contactor undergoing sequential loading and regeneration cycles.

The following factors are considered important for selection of an appropriate MSA (adapted from factors for liquid-liquid extraction for ethanol/water separation (37-40)):

1. **Selectivity** for one component relative to another. Higher selectivity results in a more concentrated regeneration product stream. This is often presented as a separation factor which is defined similarly to that of relative volatility, β , comparing the ratio of component concentrations in/on the MSA (y_i) to that in the feed material (x_i):

Equation 9

$$\beta = \frac{y_1/y_2}{x_1/x_2}$$

2. **Equilibrium distribution coefficient**, K_D , is the ratio of the concentration in the MSA material to that in the feed phase (i.e. y_i/x_i). Higher values of K_D are desirable because it reduces the amount of MSA required to remove a given mass of product with concomitant reductions in the capital and operating costs for the separation system. The separation factor is the ratio of K_D values for two compounds in the feed.
3. **Mutual solubility**. Ideally, the MSA and the bulk feed material would not be soluble in each other. Solubility of MSA in the bulk feed material results in loss of MSA from the system and may present downstream complications since the MSA could be transferred to other process steps, to the products, or to the waste treatment facility. Solubility of the bulk feed material into the MSA may alter the selectivity, capacity, and physical stability of the MSA.
4. **Ability to separate MSA and bulk stream**. Separation of the MSA and bulk feed phase is usually accomplished relying on density or other physical differences between the materials. In the cases of gas stripping and adsorption, the density differences are usually sufficient to enable easy separation of the MSA and the bulk stream. In liquid-liquid extraction with a limited density difference, gravity settling may be insufficient, requiring the use of a liquid-liquid centrifuge. In other cases, magnetic or electric forces may be used to enhance the separation.
5. **Interfacial tension**. When the two phases are in direct contact, intimate mixing is desirable, but the formation of stable or even metastable emulsions or mixed phases must be avoided. In liquid-liquid extraction where a porous membrane is used as an interfacial support, the wetting of the pores may be undesirable.

6. **MSA viscosity/flowability.** If the MSA is a liquid, a suspension of solids, or loose particles, then a low viscosity or high flowability is generally desirable since it improves mass transfer in the contactors and reduces energy required for moving and mixing the MSA.
7. **Volatility.** The desired vaporization characteristics of the MSA depend to a great extent on the regeneration scheme. If the component separated is to be recovered from the MSA by evaporation, either at ambient or at elevated temperatures, then a low volatility MSA is desirable. However, if a distillation-based regeneration scheme is employed for a liquid MSA, then some degree of volatility and a low heat of vaporization may be advantageous.
8. **Cost.** Ideally, if the MSA was completely recovered and reused, only the initial charge of MSA would be needed. Due to normal losses or chemical reactions, some amount of fresh MSA must be added periodically. Thus, the purchase of MSA represents both an upfront capital cost and an ongoing operating cost. The cost of end-of-life disposal or reprocessing of the MSA must also be considered as an operating expense.
9. **Stability/reactivity.** This factor links to several of the other factors in that degradation of the MSA necessitates replacement/reprocessing and may lead to leaching of degradation products into process streams.
10. **Lifecycle Health and Safety.** Issues of health and safety during use of the MSA should be considered when selecting an MSA. So too should lifecycle health and safety issues. For example, the MSA itself may be benign, but the method of producing the MSA or regenerating it may not. A full lifecycle assessment would identify areas of concern related to both the use and manufacture of the MSA. In bioprocesses, the MSA may inhibit the microorganisms in the bioreactor or may negatively interact with other critical bioreactor components such as enzymes. In addition, the toxicity associated with the MSA in wastewater and air releases from the production facility must be considered. Further, the flammability, flash point, and reactivity with process chemicals of the MSA and of MSA-extractant mixtures present facility health and safety issues.

The concentration of a compound removed by the MSA in the regeneration product stream is directly dependent on the selectivity of the MSA for that compound. Although higher selectivities may be possible, the regeneration product stream may still require some level of purification, depending on product specifications and the concentration of the compound in the feed stream. Unfortunately, for a given class of MSA, K_D tends to decrease as β increases. As a result, there is often a tradeoff between selectivity and amount of the MSA required to remove a given mass of a compound, particularly in the case of liquid-liquid extraction. Common methods of MSA regeneration include: vacuum flash vaporization, indirect heating, direct heating (i.e. steam, hot gas, or hot liquid), distillation, gas stripping, and membrane processing. Most of these methods simply transfer the recovered compound from the MSA to another phase or material, from which it must be separated, often by condensation, distillation, or another MSA-based method. In many scenarios, the regeneration is performed at an elevated temperature in order to increase the tendency of the compound to leave the MSA. Ideally, the distribution coefficient for compound between a gas phase (vacuum or gas) and the MSA increases significantly with increasing temperature in order to achieve as complete a regeneration as possible.

Neither the extraction nor the regeneration steps/cycles are run to completion. Thus, when the regenerated MSA is returned to the extraction contactor, or the MSA column is cycled back to extraction mode, there will be residual extracted compound in/on the MSA. This residual level must be low enough to ensure the desired level of the extracted compound in the treated stream can be reached. In this way, the extraction efficiency is linked to the regeneration efficiency, with energy demand and capital cost increasing as regeneration efficiency increases. Heat management may become a limiting design

factor in contactors due to the heat of desorption or the need to heat or cool the material/column at various stages of the process/cycle. Heat added in a thermal regeneration scheme may not be easily recoverable, especially when the heating source and the cooling sources are not naturally linked. Much of the energy and efficiency of an extraction process revolves around how efficiently the MSA can be regenerated, and this can be overlooked during the initial screening of MSA candidates.

Membrane-based Separation Processes

Finally, the *crème de la crème* of separation alternatives - membrane processes. Sustainability achieved, Earth is saved! *Non?* Membranes are often viewed as the solution for many chemical process ills, and not just by those of us in the membrane community. The truth is that membranes may be a more efficient or even more sustainable alternative in many situations, but there are limitations to membrane processes, just as there are for traditional approaches.

While membrane processes have infiltrated many process schemes, probably the most extensive replacement has been in the area of water treatment. For example, reverse osmosis has largely replaced distillation/evaporation for the production of drinking water from seawater (41, 42). Clearly, with the right mix of material properties, efficient process designs, and economic drivers, energy-efficient membrane processes can replace conventional thermally-driven separation processes. Later in this chapter, desalination will be a featured example.

The category of “membrane processes” covers a wide range of membrane-mediated processes with disparate governing principles, driving forces, and descriptive language. In general, membranes separate components in a process stream based on some combination of the size and chemical differences between those components. In the continuum of membrane processes, there are those that separate components based primarily on the size of the components and those that separate components based primarily on the molecular-scale chemical interactions between the components and the membrane material. For size-based separations, the driving force for material transport through the membrane is an applied fluid pressure gradient. Particle filtration, microfiltration, and ultrafiltration are examples of size-based membrane separations. For chemically mediated membrane separations, the driving force is the chemical potential difference between the upstream and downstream sides of the membrane. Gas separation, vapor permeation, pervaporation, reverse osmosis, and forward osmosis fall into this category. Nanofiltration spans the two. Electrodialysis adds electrical charge as a separating feature. For many of the chemically mediated membrane processes, the selective layer is a dense material and the terms “solution-diffusion” or “sorption-diffusion” are commonly used to describe transmembrane transport. In these, feed components sorb into the upstream face of the dense membrane and then diffuse through the membrane to the downstream permeate side of the membrane. The term “dense” has been used to indicate the selective material only has molecular-scale pores or transport pathways with diffusion as the primary means of movement through the membrane. Sometimes, dense membranes are referred to as “non-porous”, but this does not capture membranes with pores on the scale of small molecules, such as zeolite materials.

One of the leading voices for the opportunities and challenges for displacing thermally-driven separation technologies with membrane-based processes for improved sustainability has been Professor William Koros of the Georgia Institute of Technology. His publications on the subject are recommended reading (41, 43, 44) as is a recent review on the subject of energy-efficient gas separation membranes authored by several leading membrane researchers (45). As noted by Dr. Koros, chemically-mediated membrane processes, and hybrid technologies thereof, have great potential to displace traditional separation processes. As a result, we will emphasize these here.

In chemically-mediated membrane processes, the throughput or productivity (the rate a compound passes through the membrane) is related to the chemical potential driving force as follows:

Equation 10

$$\text{Throughput of } i = \frac{(\mu_i^{\text{Feed}} - \mu_i^{\text{Perm}})}{R_i} A = \frac{J_i A}{MW_i}$$

Where μ_i^{Feed} and μ_i^{Perm} are the chemical potentials of compound i on the feed and permeate sides of the membrane, respectively, R_i is the overall resistance to mass transfer for i , A is the membrane area, J_i is the flux of i through the membrane (e.g. kg/m²·s), and MW_i is the molecular weight. The change in chemical potential and the mass transfer resistances present for a hypothetical membrane are depicted in [Figure 6](#). As indicated, the overall mass transfer resistance is composed of three main individual mass transfer resistances situated in series: a feed-side fluid boundary layer, the membrane, and a permeate-side fluid boundary layer. The relative importance of the individual mass transfer resistances is determined mainly by the permeability and thickness of the membrane, the design of the membrane module (turbulence promoters, feed and permeate spacer layers), the feed-side flow rate, and the permeate-side flow rate. The net result is that the permeate is enriched, relative to the feed, in species which are preferentially permeated through the membrane and the feed stream becomes depleted in those same compounds. Boundary layer resistances decrease both selectivity and throughput. As a result, membrane module designs and operations are chosen to minimize these. Ideally, the membrane represents the sole mass transfer resistance (i.e. $R_i \approx R_i^{\text{Mem}}$). For gas separation, vapor permeation, and pervaporation processes, the driving force is represented by the partial pressure gradient and the inverse of the resistance is represented by the permeance (Π_i). Flux is calculated as:

Equation 11

$$J_i = \Pi_i (p_i^{\text{Feed}} - p_i^{\text{Perm}}) MW_i$$

Where permeance is the membrane permeability divided by the thickness of the selective layer (i.e. $\Pi_i = P_i/\ell$) with units of kmol/m²·s·kPa and p_i^{Feed} and p_i^{Perm} are the partial pressures of the compound on the feed- and permeate-sides of the membrane, respectively.

Membrane separation quality can be described in terms of a separation factor as defined in [Equation 9](#) with x_i and y_i representing the bulk feed-side and bulk permeate-side compositions, respectively, of two compounds being separated. However, this separation factor includes the driving forces for the two compounds and so is not an accurate reflection of the selectivity of the membrane alone. A better representation of membrane selectivity is to calculate the resistances for two compounds according to [Equation 10](#) and then calculate selectivity as the ratio of the inverse resistances. If the membrane resistance is dominant for both compounds, then the calculated selectivity would be the membrane selectivity, sometimes referred to as the permselectivity, α , defined as:

Equation 12

$$\alpha_{ij} = \frac{R_j^{\text{Mem}}}{R_i^{\text{Mem}}} = \frac{\Pi_i}{\Pi_j} = \frac{P_i}{P_j}$$

Membrane permeability is defined as the product of the solubility and diffusivity of a compound in the selective membrane layer ($P_i = S_i D_i$). Note the selectivity offered by the membrane is independent of the phase equilibrium of the system, such as the vapor-liquid equilibrium behavior.

Based on [Equation 10](#), the two ways to maximize flux are to maximize the chemical potential difference and to minimize the resistance. To minimize the membrane resistance, this means decreasing the thickness of the selective layer and/or increasing the inherent permeability of the selective material. At some point, however, improvements in membrane resistance will have diminishing impact as the other mass transfer resistances become dominant. At the material level, attempts to control the selectivity or resistance of a polymer membrane commonly encounter a trade-off between selectivity and permeability that has been often reported for permselective membranes. In other words, when researchers attempt to alter the formulation of a particular polymer to improve selectivity, it usually results in a decline in permeability, and vice versa. This is usually presented graphically as a log-log plot of selectivity vs. permeability with the extreme data values shown as a line, termed the “upper bound.” These are often referred to as “Robeson plots” and the “Robeson upper bound” in recognition of the trailblazing work of Professor Lloyd Robeson on this subject (46, 47). An example of a Robeson plot is given in [Figure 7](#) for the separation of carbon dioxide from nitrogen. This graph is a cautionary tale for anyone seeking the ideal membrane or even expecting to tweak a membrane to enhance both selectivity and permeability. The practical significance is that a high flux membrane (aka low area/low capital cost) may produce a permeate stream requiring additional processing (aka higher costs) due to the low selectivity it achieves and a high selectivity membrane producing high purity streams may require an unaffordable amount of membrane area due to the low flux inherent in the selective material.

As illustrated in [Figure 7](#), the ideal membrane with infinite selectivity and no mass transfer resistance for the preferred species (the upper right corner of the figure) does not exist. In addition, the infinite membrane area required to completely remove a target species is unaffordable. As a result, the separation performed by a real membrane system will be incomplete, yielding a permeate stream containing at least a portion of all species in the feed and a reject stream (aka “retentate”) that has not been completely rid of the preferentially permeated species. The question then becomes: can imperfect membranes be utilized to improve upon traditional separation processes? Sometimes, the answer is that the membranes are too imperfect, at least at this time, to compete. However, in many situations standalone membrane units or combinations of membranes with the traditional technology can make a significant difference. The lowest hanging fruit for applying solution-diffusion membranes have been situations where the vapor-liquid equilibrium (VLE) behavior is not favorable for distillation-based schemes. Azeotropic mixtures and close-boiling components are examples. In these cases, a membrane that can separate the two species independent of any VLE thermodynamic limitation could be used to carry out the entire separation or to at least jump the azeotrope or limiting region. Examples include azeotropic solvent/water systems like the ethanol/water or isopropanol/water systems that have azeotropes at 5 and 15 wt% water, respectively, and the close-boiling olefin/paraffin systems, such as ethylene/ethane and propylene/propane.

Another trade-off in membrane operations is the diminishing return of added membrane area. Each increment of membrane area added in series removes relatively less of the preferentially permeating species than the previous increment of membrane area and yields a reduction in the average permeate purity. Assume a gas separation membrane unit contains membrane area, A_1 , and removes 90% of compound 1 from the feed mixture. All other factors being equal, adding a second membrane unit with area A_1 will be able to remove 90% of compound 1, but that is 90% from the feed to that unit, or only an additional 9% based on the original concentration. Likewise, adding a 3rd unit of area A_1 removes only

0.9% more of the original amount of compound 1. In this unconstrained scenario, the natural log of the fraction of compound 1 remaining after treatment with a membrane system is proportional to the membrane area in the system. The reason for this is the diminishing driving force as the feed-side concentration decreases through the membrane system. Unfortunately, at the same time, the concentration of the rejected compounds remains about the same or increases through the membrane system, meaning that the driving force for transport for the rejected compound increases, leading to a higher flux of the undesired permeating species. So, not only is added membrane area less efficient at removing the preferred permeating species (based on the initial amount present), it yields a permeate stream with relatively more of the rejected species than in the first parts of the membrane system. In other words, as membrane area is increased, the purity of the rejected species increases in the retentate but the purity of the preferentially permeating species in the permeate decreases. To compensate for this situation, multiple permeate streams may be withdrawn from a membrane system and processed according to their compositions to improve on overall efficiency. Such system-wide thinking is often necessary to make an alternative process, like a membrane process, functional. An example of this will be given later for the post combustion capture of carbon dioxide.

Hybrids!

This brings us to hybrid processes. Hybrids are all the rage: be it cars, fruits, vegetables, pets, etc. But, as some curmudgeons might point out, a hybrid chemical process may just represent good process design. Rarely does a process consist of a single unit operation. So, it should come as no surprise that the most efficient separation process just might be a combination of multiple technologies. The moniker “hybrid technology” may indicate that two disparate technologies have been united, but it may also indicate that an emerging technology has been combined with an established technology. In the latter case, it designates that an emerging technology has reached a point of maturity where process designers have enough performance information or models to intelligently link it to conventional technologies. It may also indicate a level of maturity on the part of both the champions of the new technology and the guardians of the established technology to work together. In some situations, hybrids might be a low risk way of introducing a new technology – by allowing the established technology to perform most of separation, but more efficiently. As noted in the 2005 ORNL report: *“Hybrids that can be retrofit to, and easily coupled and decoupled from existing production units would provide facilities with energy improvements (and debottlenecking opportunities) without risking the normal production.”* (2) In other situations, the hybrid approach may be necessary to enable the new technology to actually be used outside the idealized world of the laboratory.

Coupling two distinct technologies to make a more efficient integrated technology is the most common type of hybrid technology. Another type is to meld two technologies into one. For example, Professor Ed Cussler’s group and his research collaborators have shown how hollow fibers can be used to significantly enhance mass transfer in a distillation column by using the hollow fibers as a non-selective structure packing (48-51). This hybrid unites the most pertinent aspect of the hollow fibers, the high surface area per unit volume, with the VLE separation characteristics of a distillation column to significantly improve efficiency. Olefin/paraffin separation is the initial target of that work. Similarly, Dr. Koros’ group has borrowed concepts from the field of hollow fiber membranes to develop high surface area adsorbents for a variety of separations including CO₂ removal from flue gas and desulfurization of natural gas (52, 53). In still another form of melded hybrid, Agrawal and Noble describe a “composite separation system” wherein two or more mass separating agents are combined in one process in a synergistic fashion (54). The example given is of combining zeolite particles into a polymer membrane to yield a mixed matrix membrane having separation performance significantly greater than that of the polymer alone, but at a cost and ease of manufacturing close to that of a polymer membrane. Thus, hybrids can

take many forms, from a simple coupling of different technologies to the alloying of different materials/structures.

4. Examples

In the preceding sections, a variety of separation processes and means of assessing energy usage or environmental impact have been presented. In this section, three specific separation challenges will be highlighted.

Example 1: Desalination

The first separation example is seawater desalination. Traditionally, desalination was done by distillation or simple evaporation/condensation (55). Today, thermally-driven desalination has been largely replaced by the membrane process reverse osmosis. In reverse osmosis, an applied pressure exceeding the osmotic pressure of the salt solution causes water to permeate through a dense membrane. Hydrated salt ions are relatively large compared to water and have a lower permeability through the membrane resulting in relatively salt-free water being collected as the reverse osmosis permeate.

A quick analysis of energy usage will indicate why reverse osmosis has replaced thermal desalination. First, [Equation 2](#) can be used to calculate the minimum work required to produce the first drop of pure water from seawater as (11):

Equation 13

$$w_{min} = -T_0 R \ln(\gamma_w x_w) = \Pi_s \bar{V}_w$$

Where Π_s is the osmotic pressure of the salt solution and \bar{V}_w is the molar volume of water. For seawater with 3.5 wt% NaCl ($x_w=0.98894$) in water at 15 °C, water activity ($\gamma_w x_w$) is 0.980 (11, 56). Thus, according to [Equation 13](#), the minimum work required to recover the first drop of water is 48.4 J/mol, more commonly reported as 2.74 kJ/kg or 0.76 kWh/m³. [Note: There is some variability in this value of minimum desalination energy reported in the literature due to different assumptions regarding the water activity. For example, if an ideal solution is assumed (i.e. $\gamma_w = 1$), then the minimum work is 45% lower (26.6 J/mol) (57)] For higher degrees of water recovery, the minimum work increases. For example, for 50% water recovery from the same seawater, the theoretical minimum increases 39% to 1.06 kWh/m³ (11). Simple thermal desalination requires 40,700 J/mol of heat to evaporate the first drop of water. Even considering the conversion of heat to work, that is a huge inefficiency for evaporation – indicating why thermal desalination is done in a multistage or multieffect process, essentially a cascade of evaporation and condensation steps at successively lower pressures to reuse the thermal energy several times over. However, if the thermal energy could be reused 5 times, the amount of thermal energy is still on the order of 8,000 J/mol. Conversely, the latest seawater reverse osmosis (SWRO) units require about 2 kWh/m³ for 50% recovery or about 127 J/mol of electrical energy, about twice the theoretical minimum for 50% recovery (11, 58). Using the 37% fuel-to-electricity efficiency referenced earlier, this translates to a primary energy usage of 344 J/mol. Adding in another 1-2 kWh/m³ for the intake, pretreatment, post-treatment, and brine discharge stages of the SWRO plant (58) still yields an SWRO primary energy requirement that is an order of magnitude lower than that of a thermally-driven process.

This largely explains why SWRO has supplanted distillation/evaporation for seawater desalination. In situations where “waste” heat is available, thermal desalination may still be economically attractive. It

should be noted that, despite an 8-fold reduction in energy required for SWRO separation since the 1970's, additional SWRO energy reductions will be harder to achieve due to proximity of current SWRO systems to the theoretical minimum (11, 58).

Example 2: CO₂ Capture

Earlier in this chapter, in the discussion of solution-diffusion controlled membrane processes, it was noted that as membrane area is added to increase the product purity of the compound rejected by the membrane, the purity of the preferentially permeating compound in the permeate stream decreases. This results in the need for clever management of multiple permeate streams and system-wide thinking. An example of this is the post combustion capture of CO₂. The conventional CO₂ capture process is amine scrubbing where the flue gas is contacted with an aqueous amine solution to sorb/complex the CO₂. The spent amine is then thermally regenerated in a stripping column, producing a concentrated CO₂ stream. The conventional amine process leads to a loss in power plant efficiency of between 15 and 29%, depending on the type of fuel and plant design (59). The low end of the range is for natural gas combined cycle plants and the high end is for subcritical pulverized coal power plants. A concerted effort is underway to develop alternatives with a lower parasitic power loss and lower cost than the conventional scrubbing process (60). In 2014, the US Department of Energy's National Energy Technology Laboratory (NETL) estimated the power penalty, per unit of CO₂ captured, for the addition of several technologies to existing pulverized coal power plants (61). At 0.249 kWh/kg- CO₂, a membrane process was 38% lower than the 2005 benchmark amine process and 22% lower than both an updated (2012) amine process and a sorbent-based process.

The membrane process for post combustion CO₂ capture uses CO₂-selective membranes to remove the CO₂ from the flue gas and yield a CO₂-rich permeate gas stream for subsequent condensation and storage. One US Department of Energy performance target for CO₂ capture is 90% CO₂ removal from the flue gas. Flue gas contains between 10 and 15 mol% CO₂. At such a high degree of removal, at that low a feed concentration, and with the general CO₂/N₂ permselectivities offered by current membranes (see [Figure 7](#)), the permeate composition from the membrane unit will be too low for efficient conversion of the CO₂-rich permeate gas into a liquid. For example, assuming a CO₂/N₂ selectivity of 50, a feed gas containing 10 mol% CO₂, and an unlimited feed to permeate pressure ratio, the permeate from the first increment of membrane area will contain 84.7 mol% CO₂. By adding enough membrane to the system to remove 90% of the CO₂, the average permeate composition would drop to 67 mol% CO₂. With a finite feed to permeate pressure ratio, this concentration would be even lower.

The first approach to this permeate purity problem is to split the membrane system into two steps (or more) with a permeate stream for each step, depicted in [Figure 8](#) as "Option 1". The permeate stream from the first step, the richest in CO₂, would be processed to make it a pipeline-ready liquid. The permeate from the second step, enriched relative to the feed stream but not high enough for economical processing for pipeline transport (i.e. >95% CO₂), is recompressed as a gas and returned to the feed stream of the first membrane step in order to retain the CO₂ in the system. An alternative, system-wide, process concept, integrating the membrane separation system with the larger power plant, Option 2 in [Figure 8](#), was proposed by Merkel *et al.* from Membrane Technology and Research, Inc. (62). Instead of the membrane system operating independently of the power plant, this alternative utilizes the combustion air as a countercurrent permeate sweep gas in the second membrane step. This accomplishes several things. Firstly, it replaces the vacuum compressor of the original 2-step design, instead purging the permeate zone of the second membrane step with air already destined for the burner, saving on both energy and capital costs. Since the sweep air has minimal CO₂ and is operated in a countercurrent mode, it yields a higher driving force for mass transfer than did the

vacuum, thereby greatly reducing the membrane area required in the second step. The CO₂ in the air sweep stream passes through the burner and is returned to the first membrane step. Process simulations by Merkel *et al.* predicted that the air sweep option (“Option 2” in [Figure 8](#)) would require 57% less membrane area, 33% less power, and have a 41% lower cost of capture than the original 2-step design with vacuum on the 2nd step (“Option 1”) (62). Another interesting facet of the analysis is that a membrane selectivity greater than 50 is predicted to yield minimal cost savings. The largest cost reduction would result from increasing the CO₂ permeance. This has been noted for other membrane separations: above a threshold selectivity, overall process cost is relatively constant. As a result, improvements in selectivity are not always worth pursuing, particularly considering the selectivity-permeability tradeoff noted earlier.

Example 3: Solvent/water separation

As highlighted by the ORNL and NRC reports from 2005 cited in the first section (2, 3), alternatives to distillation are needed for the recovery of organic compounds from aqueous solutions, particularly those forming azeotropes and in dilute aqueous solutions. The dilute nature of the feed means the minimum work to perform the separation is high. Worse, the second law efficiency of distillation in these cases is low. Even worse, the presence of an azeotrope requires introduction of an extra separation process or agent to accomplish the full separation. This opens the door to alternatives that save energy or are not limited by an azeotrope – or both.

In this example, a hybrid vapor stripping-vapor permeation process studied by the author will be discussed as an alternative to conventional distillation for alcohol/water separation (Shameless self-promotion alert!). In the US, the standard process for recovering ethanol from a corn starch fermentation broth and drying it to meet fuel specifications is a process combining distillation with molecular sieve adsorption, as illustrated in [Figure 9](#). A stripping column removes the ethanol from the broth, achieving high levels of ethanol recovery (i.e. low residual ethanol in the bottoms stream). The ethanol-enriched overhead vapor from the stripping column is then sent to a second column, a rectification column wherein the ethanol is enriched to near the ethanol/water azeotrope of 95.6 wt% ethanol. The near-azeotropic overhead product from the rectification column is then dried in an adsorption step using beds of water-selective zeolite beads operated in loading/regenerating cycles. The 2nd Law efficiency of the conventional approach was estimated to be only 5-9% for a fermentation broth containing 10 wt% ethanol (10). Clearly, there is room for improvement. For a discussion of alternatives for alcohol recovery and drying, a recent review article by this author is recommended (as promised, shameless) (40).

It should be noted that the current “conventional” approach for ethanol/water separation supplanted heterogeneous azeotropic distillation wherein a third compound, commonly benzene, was added to break the water/ethanol azeotrope (63). The health and environmental concerns associated with benzene and other entrainers prompted investigation of alternative ethanol drying approaches. Advances in both zeolite adsorbents and process design made molecular sieve drying a viable alternative to azeotropic distillation. Molecular sieve drying of fuel ethanol had become a demonstrated commercialized technology not long before the corn-to-ethanol boom in the US, allowing this separation technology to become the standard in that market.

As in the previous examples of applying membranes in desalination and carbon dioxide capture, membrane processes are promising options for alcohol/water separations (40, 64). For the recovery of the alcohol from dilute fermentation broths, hydrophobic pervaporation membranes could be applied instead of distillation. For the final drying step, pervaporation or vapor permeation with water-selective

membranes could compete with molecular sieve adsorption and even rectification. However, as has been noted previously, membrane systems lose efficiency when high recoveries are required – as would be necessary to compete with the high ethanol recoveries of the stripping column of the distillation scheme in [Figure 9](#). Thus, a hybrid of distillation with a membrane would seem appropriate when high recoveries are needed. One such hybrid has been under development by the author's group, in collaboration with Membrane Technology and Research, Inc., the same company previously mentioned in the CO₂ capture example (65-72). The schematic of such a process, termed "Membrane Assisted Vapor Stripping" (MAVS), is shown in [Figure 10](#).

The stripping column in the MAVS process serves the same function as in the traditional distillation/adsorption scheme; it provides high alcohol recovery and a low effluent concentration. The main difference is that the thermal energy to drive the stripping column is provided by recovering the latent and sensible heat from the overhead vapor leaving the stripping column. Little or no additional reboiler heat is required. First, the overhead vapor is compressed so that it can be fractionally condensed in a dephlegmator – essentially a high surface area heat exchanger with multiple VLE stages – at a temperature sufficient to transfer the heat of condensation to the reboiler of the stripping column. The water-rich condensate formed in the dephlegmator is returned to the top of the stripping column. Just a few stages of VLE are needed in the dephlegmator to substantially enrich the vapor, although the most efficient and/or cost-effective design may result in significant concentrations of water remaining in the alcohol-enriched overhead vapor. This dephlegmator overhead vapor is further compressed prior to directing the stream to the vapor permeation membrane steps for further water removal. The higher total pressure provides a higher partial driving force for solution-diffusion mass transfer through the membrane. Water-selective membranes are utilized in both membrane steps. The water-rich permeate stream from the first membrane step is returned directly to the stripping column to form a portion of the stripping vapor. Depending on the desired water concentration in the final alcohol product, the second membrane step may require a lower permeate pressure to operate efficiently. This lower permeate pressure can be achieved by vapor compression (as in [Figure 10](#)) or by condensation. Either way, the 2nd step permeate stream is returned to the stripping column or dephlegmator, although at a higher stage than the 1st step permeate due to a higher alcohol concentration.

The MAVS process largely replaces the thermal energy requirement of the traditional distillation/adsorption process with the shaft work of the vapor compressors. Recalling the discussion of mechanical vapor recompression heat pumps earlier in this chapter, there are certainly parallels between MVR and the vapor compression-fractional condensation-heat recovery portion of the MAVS process. Therefore, the logical question is: Does this swap actually save primary energy usage? The answer is presented in [Figure 11](#). In this figure, the primary energy required per kg of 99.5wt% ethanol product for a conventional distillation/adsorption process, a MAVS process, and the theoretical minimum work scenario are presented as a function of the concentration of ethanol in the feed stream to the separation process. As described earlier, the efficiency of converting primary energy to heat and of converting primary energy to electrical energy was assumed to be 85% and 37%, respectively. For the MAVS process, the efficiency of converting electrical energy into compression work was assumed to be 75%. The curve for distillation/adsorption was established from literature references (40, 73-77). The thermal energy added by the molecular sieve section of the distillation/adsorption process was assumed to be 1.5 MJ/kg-product, the mid-point of the range reported. The MAVS process was simulated using ChemCAD 6.5.5 process simulation software with spreadsheet calculation modules for the membrane units as described in previous publications from the author's group (self-citation: the highest form of self-flattery?) (66, 78). The minimum work was calculated according to [Equation 2](#) assuming

the bottoms stream from the stripper and the ethanol product are pure water and pure ethanol, respectively, and calculating activity coefficients for the feed stream using the NRTL thermodynamic model in ChemCAD. Minimum primary energy was then calculated from the minimum work using a 37% conversion efficiency.

The low 2nd Law efficiency of distillation/adsorption is apparent from the difference between the primary energy usage curves in [Figure 11](#) ~~Figure 11~~. According to the values in the figure, for a 10 wt% feed, the traditional process has a 2nd Law efficiency of only 7.0%. That value is exactly in the middle of the range cited earlier for distillation/adsorption for the same separation (10). That efficiency falls to 6.4% and 3.3% as the feed concentration is reduced to 5 wt% and 1 wt%, respectively. By comparison, the 2nd Law efficiency of the MAVS process is over three times that of distillation/adsorption, 24.3% efficient for a 10 wt% ethanol feed, falling to 21.4% and 10.8% for 5 wt% and 1 wt% feeds, respectively. The lower heating value (LHV) of ethanol is 27 MJ/kg. Thus, for a 1 wt% ethanol feed, the amount of energy required by traditional distillation/adsorption for the same feed approaches the LHV content of the produced ethanol. On the other hand, the MAVS process uses only 24% of the LHV of ethanol to perform the separation, despite a 2nd Law efficiency of 10.8% at such a low feed concentration, demonstrating the potential for an alternative scheme to improve efficiency and expand the range where alcohol recovery is, at least, a net energy winner.

5. Concluding thoughts

While there is a clear need for low-energy alternatives to thermally-driven separation processes, advancing low-energy separation technologies depends on the availability of mass separating agents that achieve selective separations and cost effective process options. As noted in the 2005 NRC report (3): “While membrane separations, adsorption, and extractions tend to be less energy intensive [than distillation], significant technical challenges must be overcome in the development of these alternatives in order to realize any significant reductions in energy intensity of the chemical process industry.” The ORNL report echoed that sentiment and identified the following needs for materials/equipment of low energy processes in order for them to be implemented (2):

1. provide the selectivity required;
2. provide the throughput required;
3. provide adequate throughput for long periods of time;
4. be sufficiently durable to maintain optimum performance under harsh environments;
5. provide sufficient economies-of-scale incentive for large-volume processes.

One reminder for those of us who think we have built a better mouse trap: traditional technologies are not static. A quick look at the advances in distillation technology over the years will prove it (79). The same economic, energy, and environmental pressures that motivate searches for alternative technologies also stimulate advances in the conventional technologies, as does the competition posed by the nascent alternatives. However, as shown in the desalination example, it is possible to develop and commercialize an alternative with a high thermodynamic efficiency. Conversely, the alcohol/water separation example indicates that there is still room for improvement. One such opportunity is combining a lower energy alternative, like a membrane process, with renewable energy (80). Caution is needed because “renewable” does not necessarily mean “sustainable” or “economical”, just as “waste heat” is not free – there is always a cost to capture and move that heat.

On a final note, this chapter has been about separating things, but the reverse process, the controlled mixing of streams, is being considered as a means to take advantage of Mother Nature's tendency to mix things up. For example, both pressure retarded osmosis (PRO) and reverse electrodialysis (RED) use permselective membranes to recover energy from the controlled mixing of seawater with a low salinity stream, such as river water or a wastewater treatment effluent (81). In PRO, the two streams are separated by a membrane that selectively allows water to flow from the dilute stream to the high salinity stream, creating a hydraulic head on the salty side that can then drive a turbine (82, 83). In RED, alternating cation and anion exchange membranes separate the saline and low salinity streams allowing ions to flow from high to low salinity creating an electrical current (84). Here, the lunch may not be completely free, but at least it is a "downhill" task.

Disclaimer: The views expressed in this chapter are those of the author and do not necessarily reflect the views or policies of the U.S. Environmental Protection Agency.

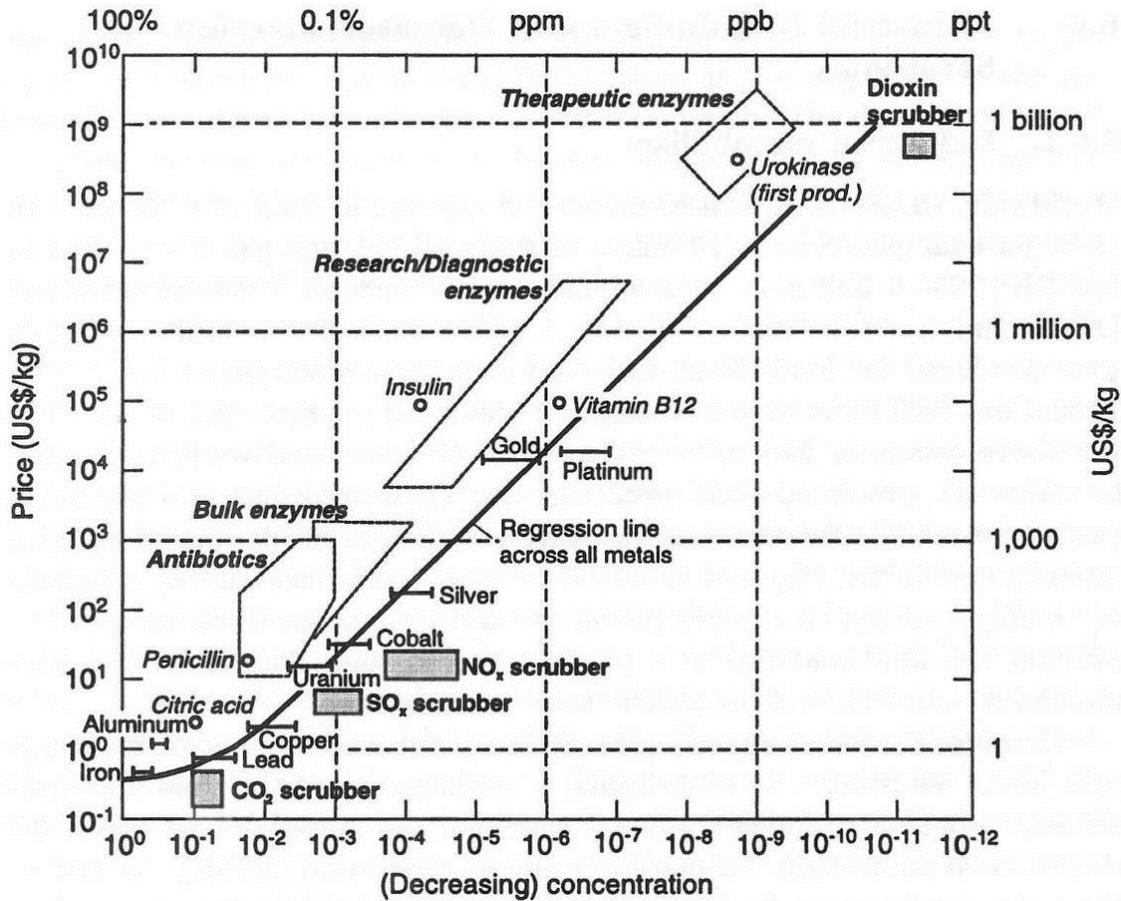


Figure 1. Sherwood plot of material selling price as a function of the concentration of the material in the initial matrix [Reproduced from "Technology and Global Change" (1), Cambridge University Press]

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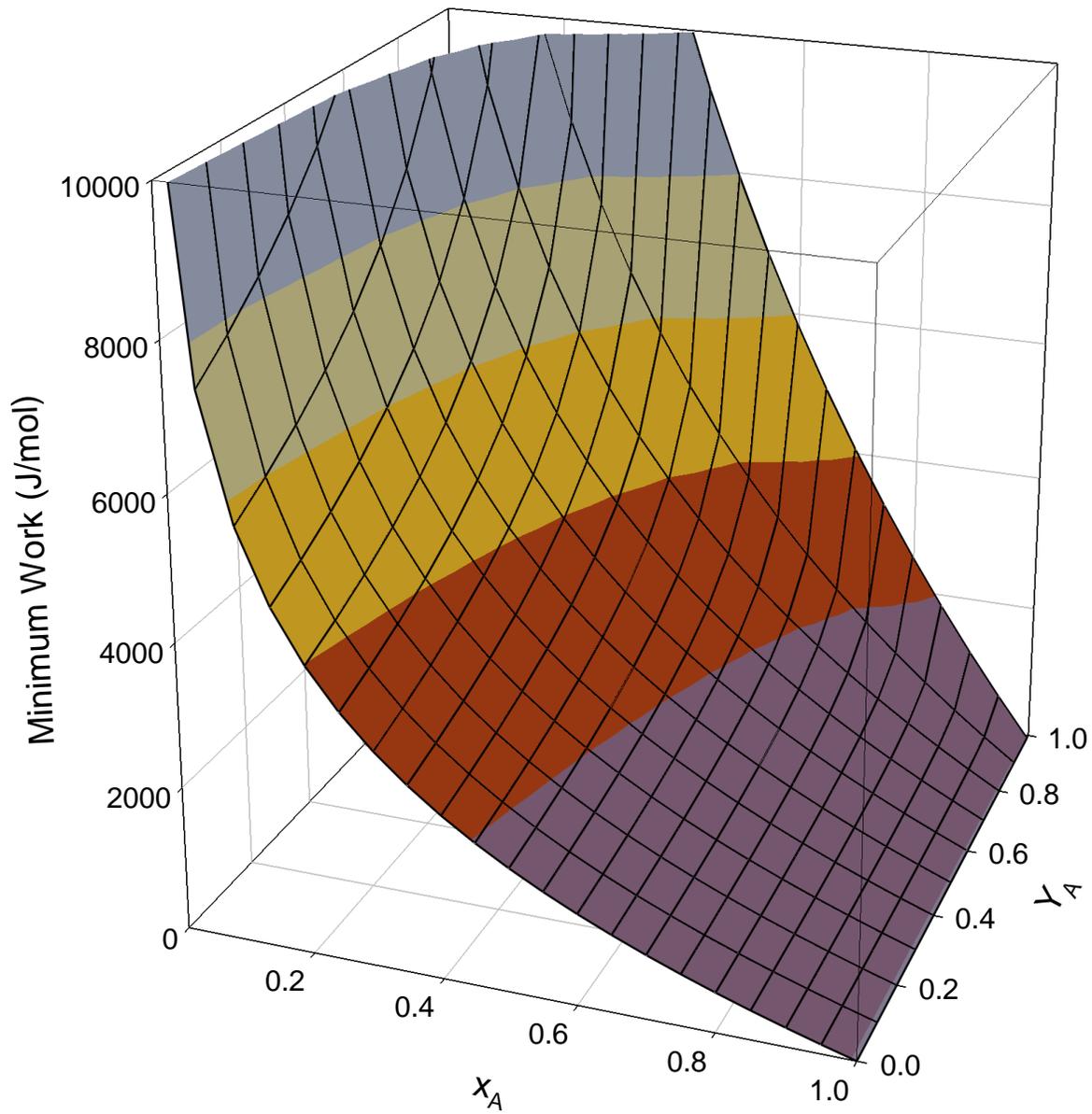


Figure 2. Effect of concentration (mole fraction of A) and fraction of A recovered on the minimum work required per unit of pure component of A produced from an ideal binary mixture.

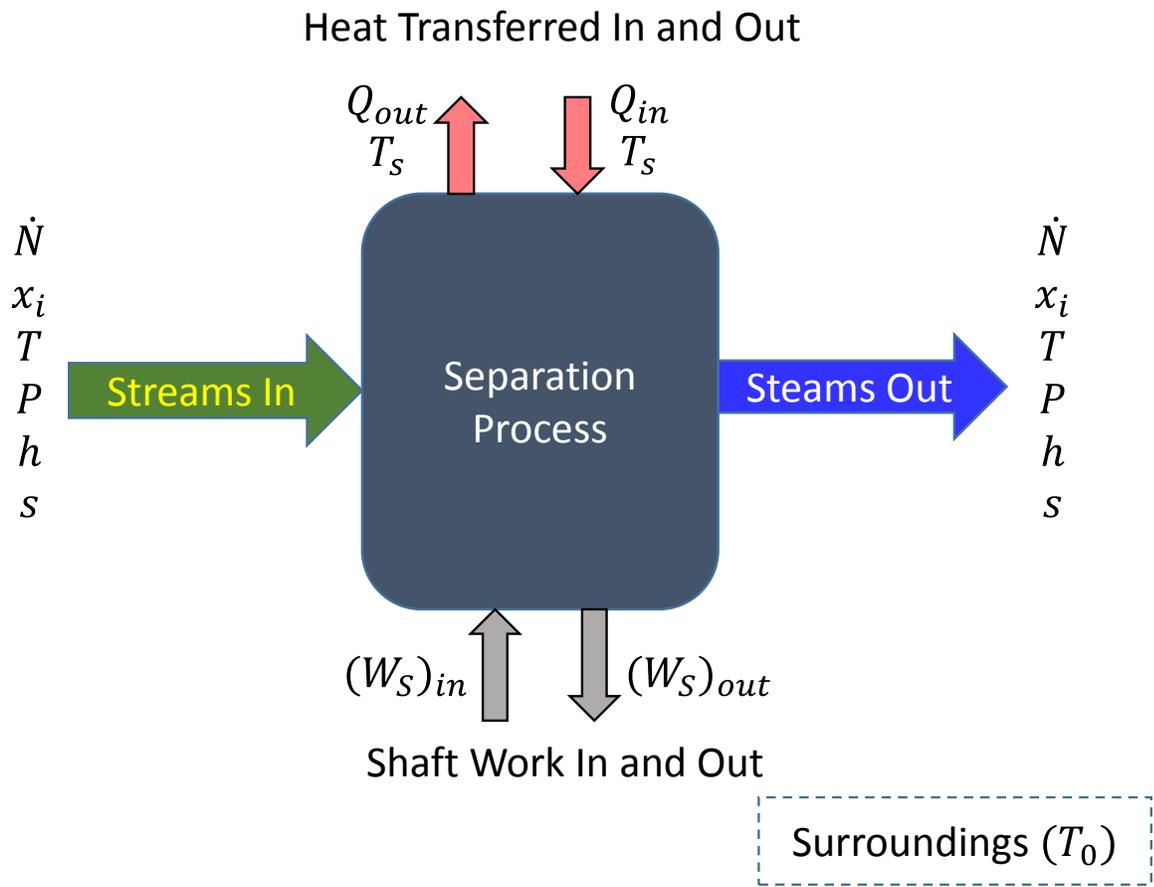


Figure 3. Schematic of a generic separation process

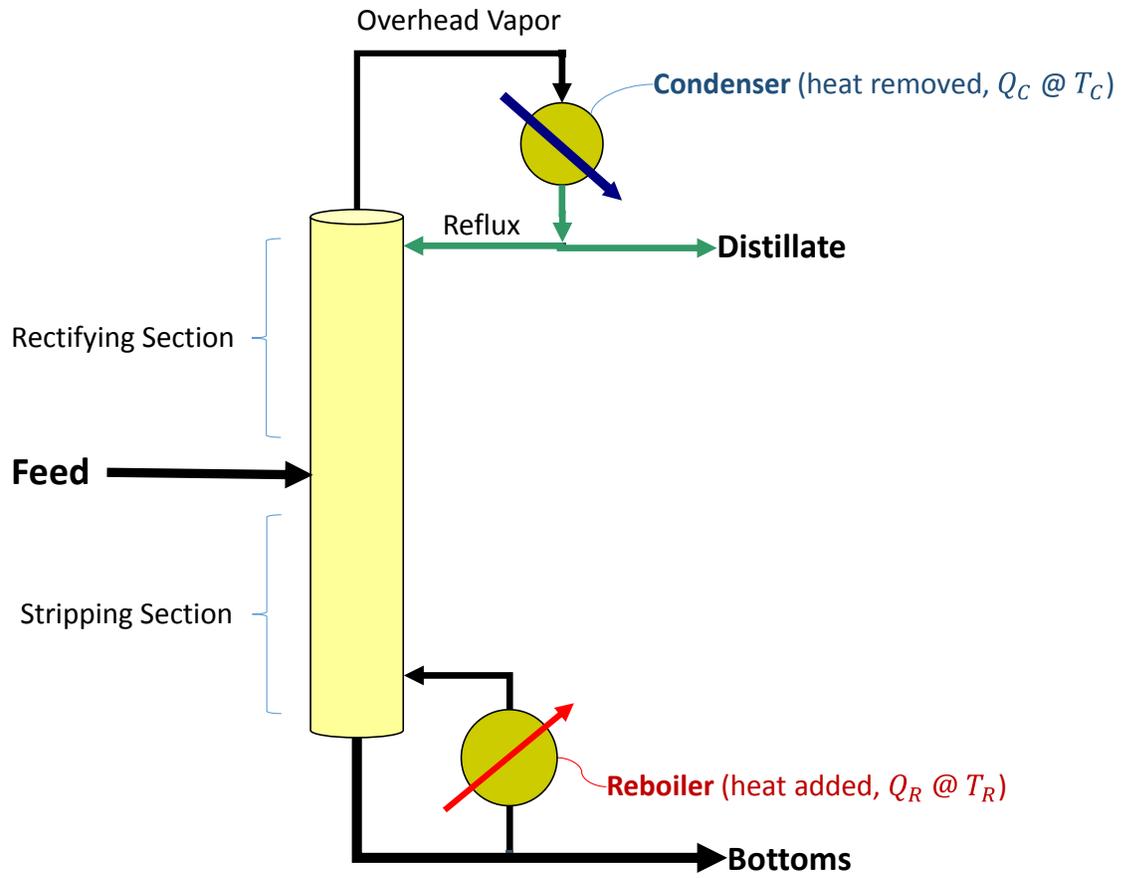


Figure 4. Simplified schematic of a distillation column.

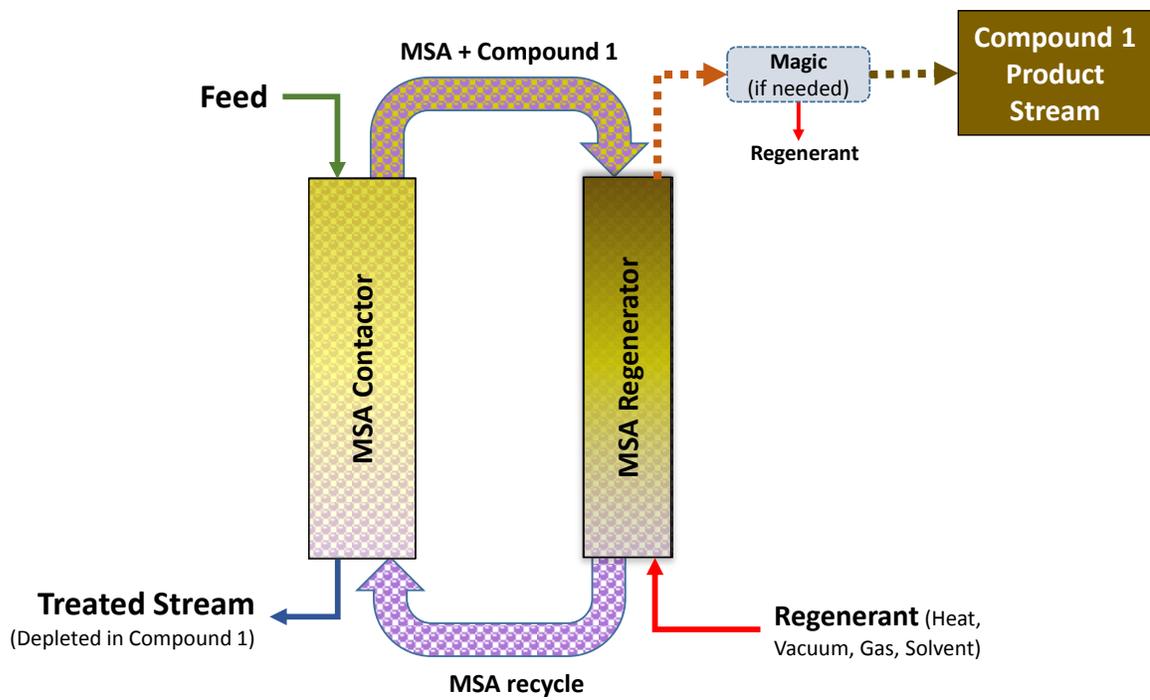


Figure 5. Illustration of continuous extraction process using a mass separating agent (MSA).

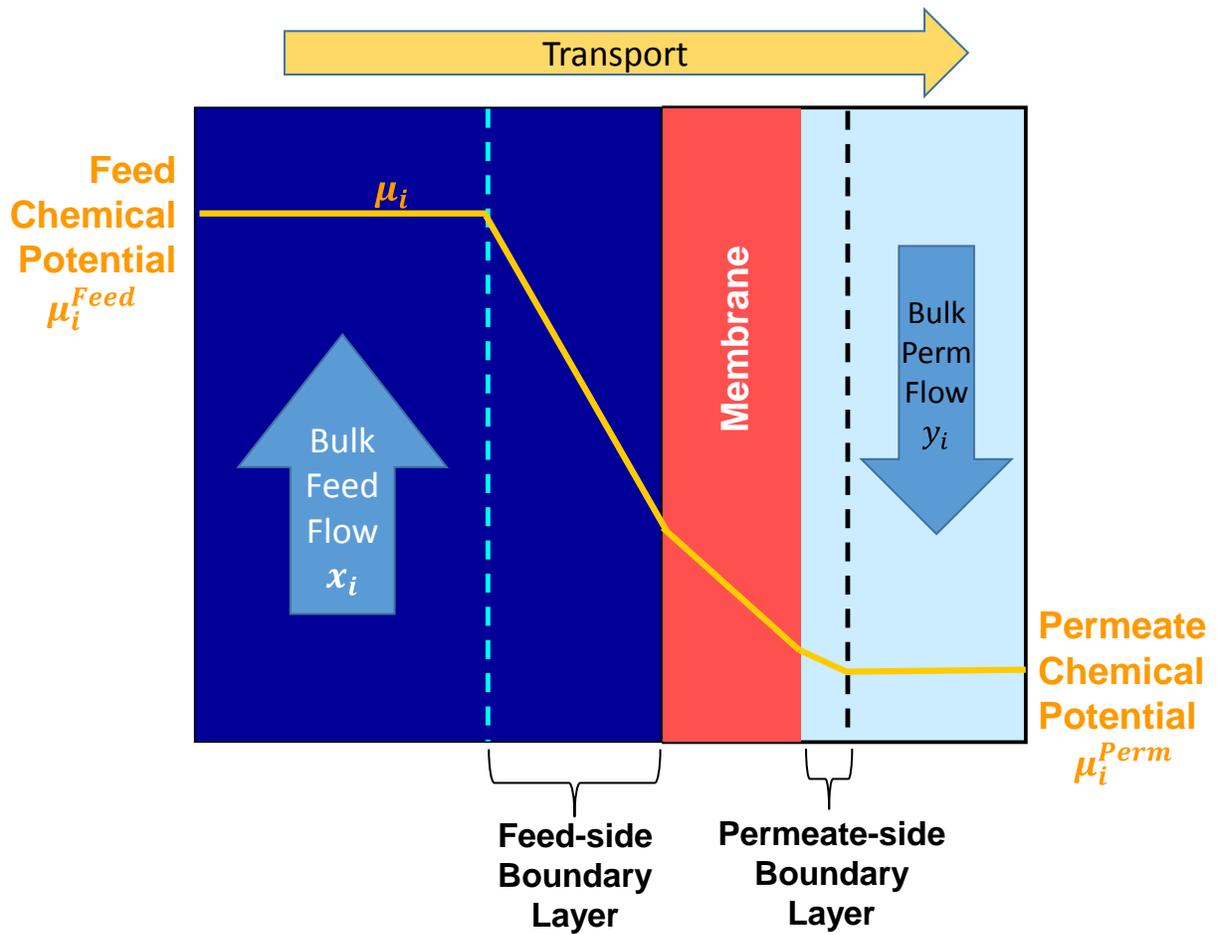


Figure 6. Mass transfer in a chemically-mediated membrane process. The chemical potential gradient from the bulk feed to the bulk permeate streams is the driving force for mass transfer (shown as yellow line). Three main resistances to mass transfer are shown – fluid boundary layers on the feed and permeate sides of the membrane and diffusion through the membrane.

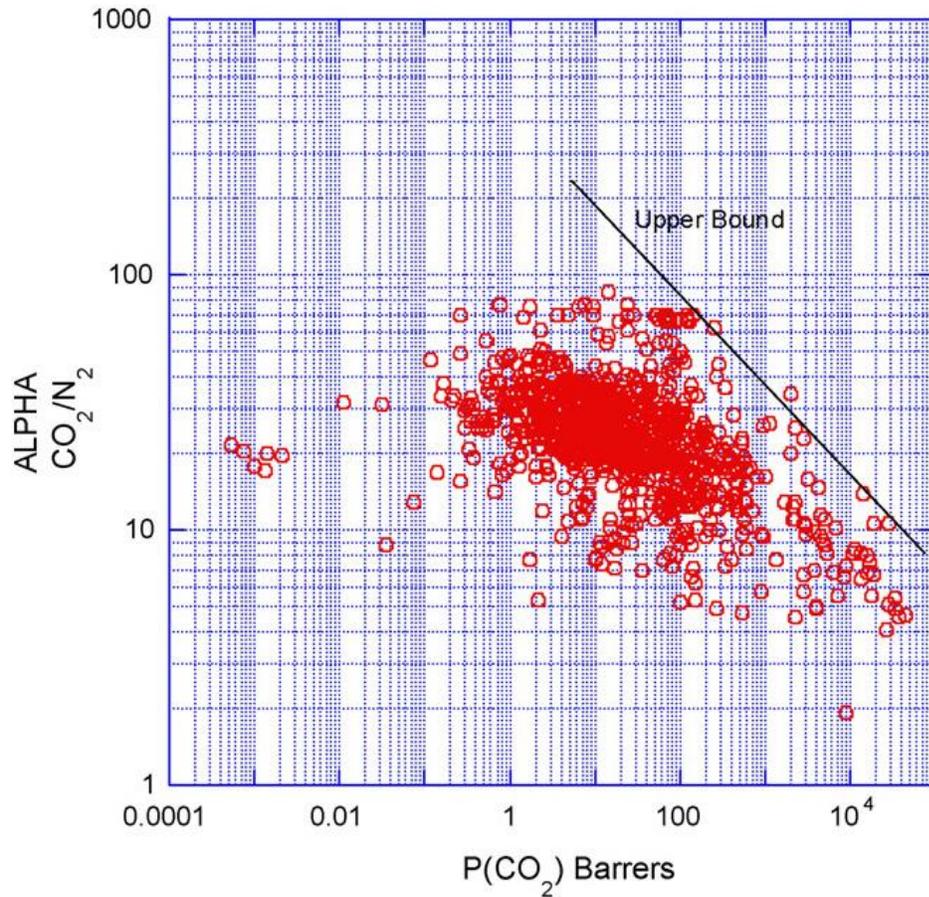


Figure 7. Robeson plot illustrating the tradeoff between selectivity (α , ALPHA) and permeability (P) for the separation of carbon dioxide from nitrogen with polymer membranes (47). The circles indicate all literature data considered relevant. The upper bound line is an empirical judgment of the outermost range of reliable data. [Reprinted from *J. Membr. Sci.*, **320**(1-2), L. M. Robeson, "The upper bound revisited", pp390-400, Copyright (2008), with permission from Elsevier].

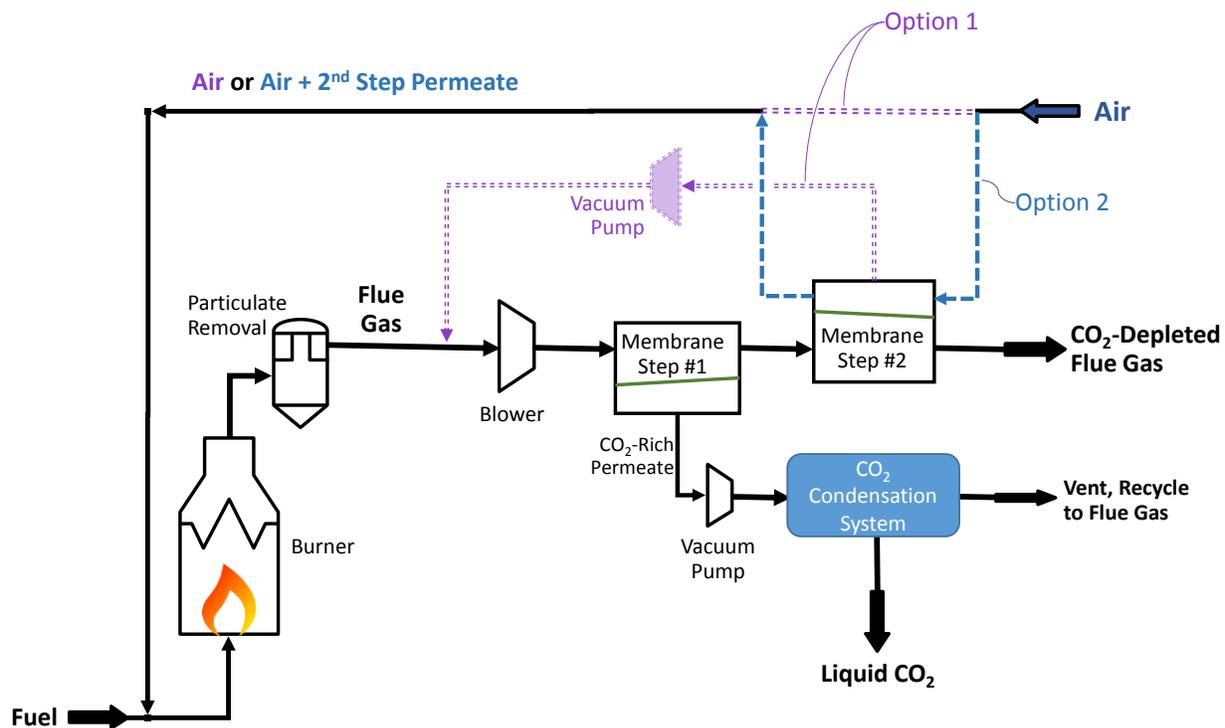


Figure 8. Example of carbon dioxide separation from power plant flue gas using a 2-step membrane process with two options for managing the permeate from the second membrane step. In Option 1 (purple double-dotted lines), air is used directly in the burner while a vacuum pump creates partial pressure driving force in the 2nd membrane step with return of the 2nd step permeate to front of membrane process. In Option 2 (blue dashed lines), the combustion air is used as a countercurrent permeate sweep gas in the 2nd membrane step. Adapted from Figures 11 and 12 in Merkel et al. (62).

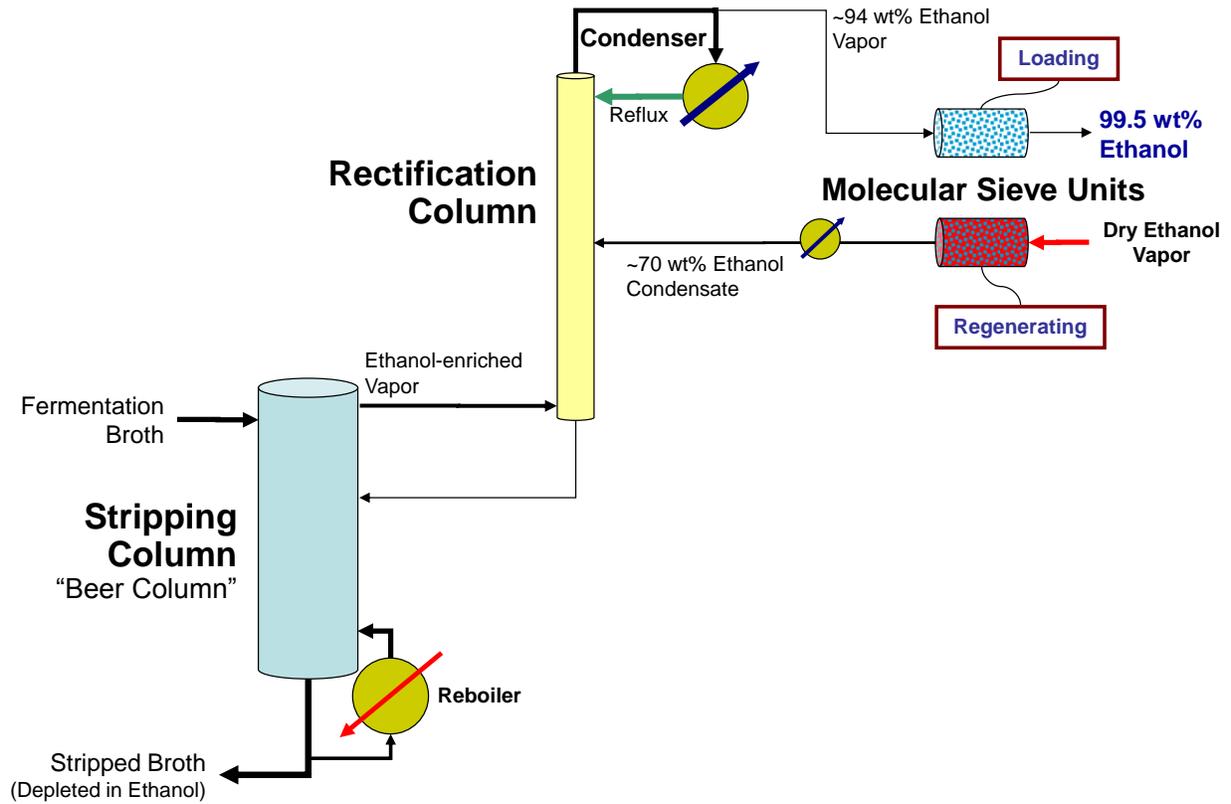


Figure 9. Schematic of traditional ethanol recovery and drying process for a corn-to-ethanol facility. Feed/effluent heat recovery exchanger on stripping column not shown.

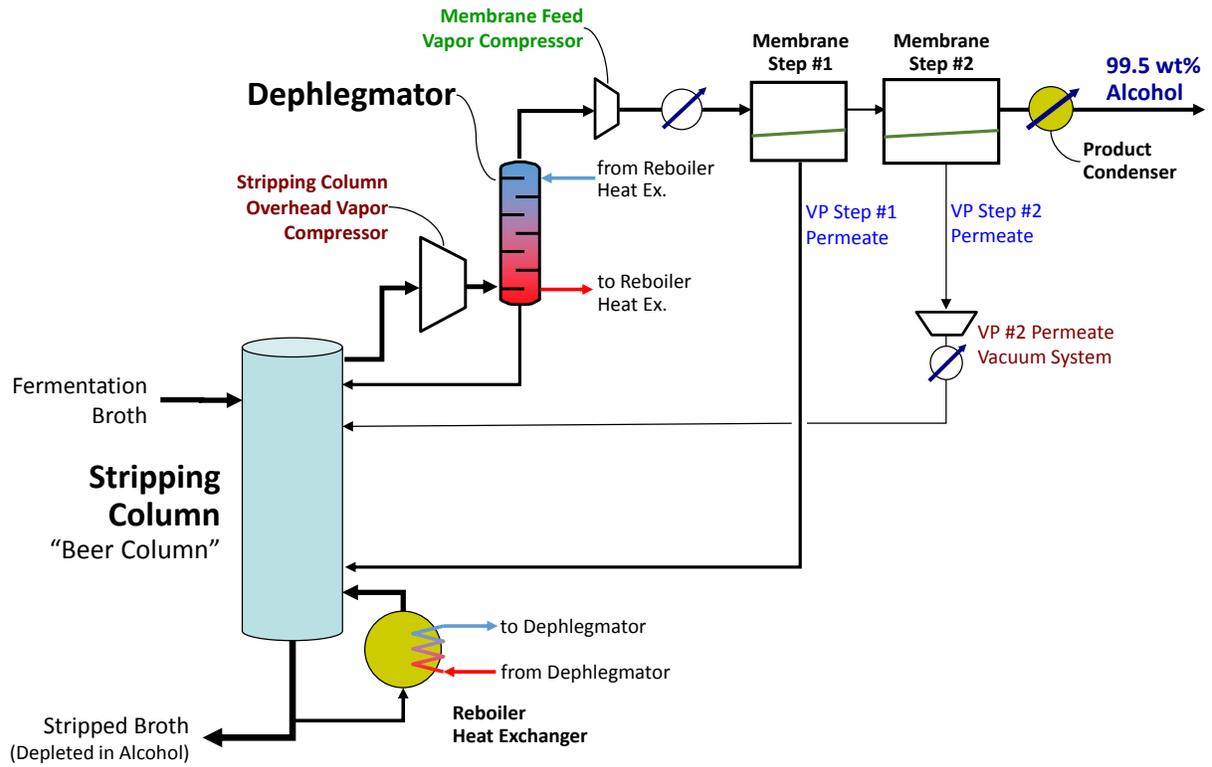


Figure 10. Schematic of hybrid vapor stripping-membrane vapor permeation process ("Membrane Assisted Vapor Stripping") process for recovering and drying alcohols from water. Feed/effluent heat recovery exchanger on stripping column not shown.

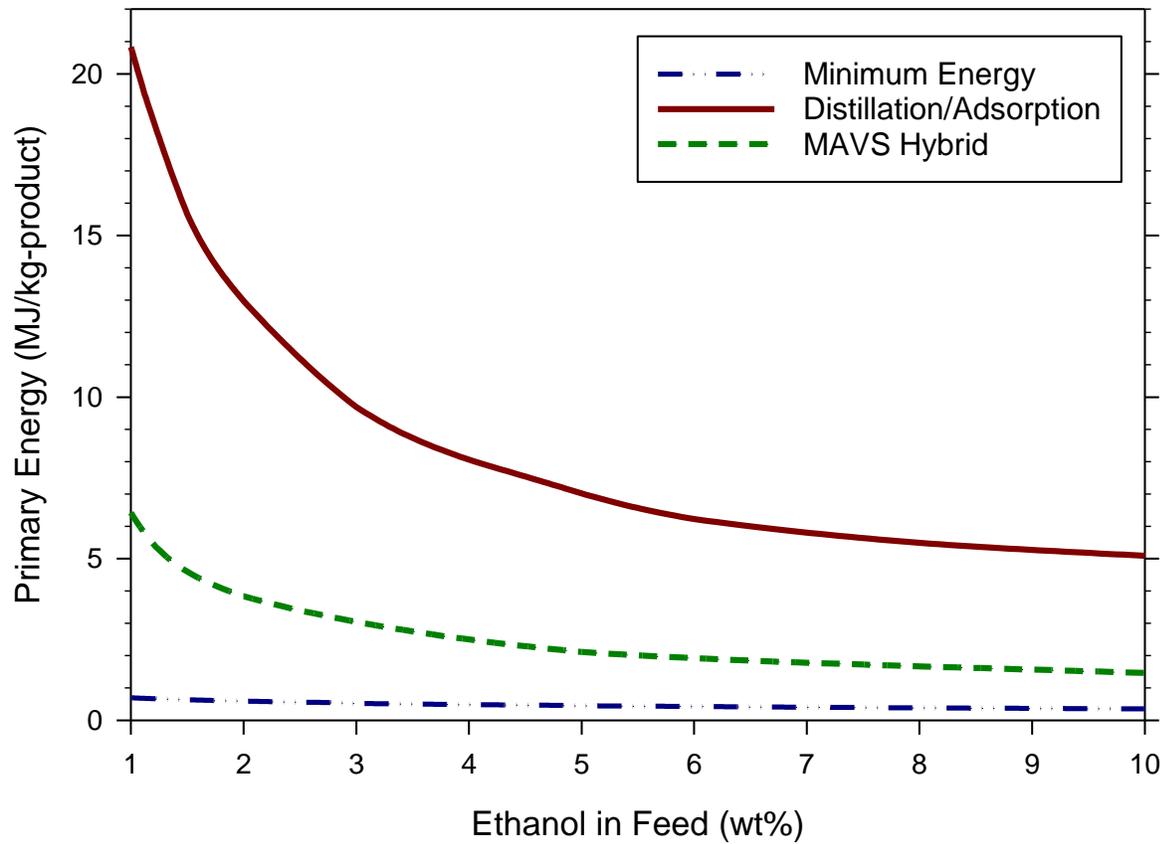


Figure 11. Comparison of the primary energy usage for ethanol/water separation using traditional distillation/adsorption process (Figure 9) and hybrid Membrane Assisted Vapor Stripping (MAVS, Figure 10) process. Minimum energy (from minimum work calculation) shown as reference. Assumptions: 37% and 85% efficient conversion of primary energy to electrical energy and thermal energy, respectively, 0.02 wt% ethanol in stripping column bottoms, and 99.5 wt% ethanol product (0.5 wt% water).

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